

## ADDITIVE FOR RUBBER ELASTOMERS

### BACKGROUND OF THE INVENTION

This application is a continuation-in-part of application US Serial No. 10/395,941, filed February 6, 2003.

This invention is directed to an additive/process aid for polymeric materials such as rubber elastomers. More particularly, this invention is directed to an additive/process aid for such polymeric materials to facilitate the processing and/or enhance the properties of the elastomers.

Polymeric materials such as rubber elastomers are used for the manufacture of various products including tire components such as tire tread, wedge compounds, sidewalls, bead filler and tire carcasses. However, it is well known that rubber elastomers tend to exhibit certain undesirable physical characteristics, such as, poor tear strength.

Tear strength or crescent tear is a measurement of the resistance of a material to tear forces. The higher the crescent tear measurement, the more difficult it is for the elastomer to be torn from whatever it is bonded to, such as steel.

Rubber elastomers also tend to exhibit weak tensile strength. Tensile strength is a measurement of the force at which a rubber elastomer can be expected to fail under a tension load. The tensile strength of the rubber elastomer is important in order to maintain its elasticity. Specifically, for rubber elastomers used in tires, the higher the tensile strength, then the more air pressure can be added to the tire, without fear of blowing the tire.

1        Finally, rubber elastomers tend to have a low  
2        elastic limit or tan delta measurement. The tan delta  
3        measurement is a measurement of the stress and strain  
4        exhibited on the elastomer or the amount of force that  
5        can be applied before the elastomer reaches its elastic  
6        limit and fails. It is advantageous for numerous  
7        applications to increase the elastic limit of rubber.

8        With particular regard to tire applications, it is  
9        desirable to produce rubber elastomers or elastomeric  
10       materials capable of exhibiting reduced hysteresis.  
11       Such rubber elastomers when fabricated into components  
12       for constructing articles such as tires, vibration  
13       isolators, power belts, and the like, will display  
14       properties of increased rebound, decreased rolling  
15       resistance and reduced heat-buildup when subjected to  
16       mechanical stress during normal use. Hysteresis refers  
17       to the difference between the energy applied to deform  
18       an article made from the elastomer and the energy  
19       released as the elastomer returns to its initial, un-  
20       deformed state. In pneumatic tires for instance,  
21       lowered hysteretic properties are associated with  
22       reduced rolling resistance and reduced heat build-up  
23       during operation of the tire. These properties, in-  
24       turn, result in lowered fuel consumption of vehicles  
25       using such tires and prolonged tire life. A reduction  
26       in the measured tan delta of the elastomer is  
27       indicative of a reduction in the hysteresis of the  
28       elastomer.

29       To address these undesirable physical  
30       characteristics, process aids and/or additives were  
31       introduced into the rubber elastomer composition.  
32       Process aids are substances added to aid in the  
33       production processing of the rubber elastomers.

1 Additives are substances added to improve specific  
2 physical characteristics of the rubber elastomer.  
3 Additives can also act as process aids and aid in the  
4 processing of the elastomers.

5 Additives, such as calcium stearate and stearic  
6 acid, were used as process aids. However, the  
7 organic/organometallic nature of these substances  
8 causes them to have limited thermal stability and shelf  
9 life. Other prior process aids were products of  
10 organic chemical reactions. However, these process  
11 aids were not reproducible batch after batch and were  
12 often prone to error. Additives, such as carbon blacks  
13 and various silicas, were also added to improve, among  
14 other things, the tensile strength of rubber  
15 elastomers.

16 Thus, there is a need for a process aid which  
17 overcomes the limitations of the prior additives, and  
18 is a simple, low-cost product that improves the  
19 physical characteristics of rubber elastomers by  
20 providing increased tensile strength, elasticity and  
21 tear strength.

#### 22 SUMMARY OF THE INVENTION

23 In accordance with the present invention, there is  
24 provided an additive/process aid for polymeric  
25 materials such as rubber elastomers which overcomes the  
26 limitations of earlier additives/process aids.

27 Further, in accordance with the present invention,  
28 there is provided an additive/process aid which  
29 provides a simple, quick, and low-cost, slow speed  
30 mixture blend which produces a stable product. It also  
31 improves the physical characteristics of rubber  
32 elastomers, by providing, among other things, increased  
33 tensile strength, elasticity, and tear strength.

1       The additive/process aid comprises a mixture of  
2 comminuted or micronized shale/slate predominately  
3 formed of aluminum, magnesium and/or iron silicates,  
4 starch, a reactive resin component, a metal carbonate  
5 and an acidic component such as a fatty acid or a  
6 silica gel.

7       As used herein, comminuted shale/slate includes  
8 gray slate flour (alumina silicate or ground shale) as  
9 well as silicates of aluminum, magnesium and iron and  
10 mixtures thereof. The gray slate flour is typically in  
11 powder form to assist in its dispersion in the  
12 polymeric material.

13       Starch may be obtained from most agricultural  
14 crops; the dominant starch raw materials being potato,  
15 cassava, corn and wheat. Corn starch is preferred and  
16 the present invention is described with particular  
17 reference to the use of the same.

18       The resin component is selected from the group of  
19 reactive polyesters resins and epoxy resins. The  
20 reactive cite of the polyester resin may comprise a  
21 carbon-carbon unsaturation intermediate ester groups.  
22 Preferred polyesters include those used in structural  
23 applications such as reinforced laminates. The epoxy  
24 resin may comprise a wide range of epoxies as described  
25 below, but epoxidized soybean oil is preferred.

26       The metal carbonate preferably includes a metal  
27 selected from Group IA or IIA of the Periodic Table.  
28 Calcium carbonate is preferred and described below.

29       The acidic component may comprise silica gel or a  
30 fatty acid. Useful fatty acids include stearic acid  
31 and oleic acid.

1       The additive may be formulated with reduced  
2 amounts of metal carbonate and increased amounts of the  
3 remaining ingredients varying up to about: 30% flour,  
4 35% starch, 15% resin, 5% metal carbonate and 15%  
5 acidic component, by weight, wherein the aggregate  
6 amount of the ingredients total 100%. On the other  
7 hand, the metal carbonate may be increased and the  
8 remaining ingredients reduced to about: 10% flour, 10%  
9 starch, 5% resin, 70% metal carbonate and 5% acidic  
10 component, by weight, wherein the aggregate amount of  
11 the ingredients total 100%. Additive/process aids  
12 having these "high" and "low" formulations have  
13 provided improvements with acceptable trade-offs in  
14 certain of the composition properties readily  
15 identified by the skilled compounder.

16       In preferred compositions, the additive/processing  
17 aid comprises from 10 to 30% shale/slate material, 10  
18 to 35% starch, 5 to 15% resin, 10 to 40% metal  
19 carbonate, 5 to 15% acidic component, by weight,  
20 wherein the aggregate amount of the ingredients total  
21 100%. More preferably, the additive/processing aid  
22 comprises from 20 to 30% shale/slate, 20 to 35% starch,  
23 5 to 10% resin, 20 to 35% metal carbonate, 8 to 15%  
24 acidic component, by weight, wherein the aggregate  
25 amount of the ingredients total 100%.

26       Preferred additive/processing aid compositions  
27 including polyester resin and silica gel comprise from  
28 20 to 29% gray slate flour, 18 to 28% corn starch, 4 to  
29 8% liquid polyester, 10 to 20% calcium carbonate, 8 to  
30 15% silica gel, by weight, wherein the aggregate amount  
31 of the ingredients total 100%. More preferably, the  
32 additive/processing aid contains about 29% gray slate  
33 flour, about 28% corn starch, about 8% liquid

1 polyester, about 20% calcium carbonate, about 15%  
2 silica gel, by weight, wherein the aggregate amount of  
3 the ingredients total 100%.

4 Preferred additive/processing aid compositions  
5 including epoxy resin and a fatty acid comprise from 20  
6 to 30% gray slate flour, 20 to 35% corn starch, 5 to  
7 10% epoxy, 10 to 20% calcium carbonate, 10 to 15% fatty  
8 acid, by weight, wherein the aggregate amount of the  
9 ingredients total 100%. More preferably, the  
10 additive/processing aid contains about 25% gray slate  
11 flour, about 25% corn starch, about 5% epoxy resin,  
12 about 35% calcium carbonate, about 10% fatty acid, by  
13 weight, wherein the aggregate amount of the ingredients  
14 total 100%.

15 As noted above, the resin may comprise a polyester  
16 resin or an epoxy resin. The resins are preferably  
17 liquid at rubber processing conditions and have a  
18 molecular weight of from about 200 up to about 10,000  
19 or higher.

20 Suitable epoxy compounds comprise molecules having  
21 at least one or more epoxide group per molecule and  
22 include epoxidized alkanes, alkenes, cycloalkanes,  
23 alkenes and other epoxidized polymers and chemicals.  
24 For example, epoxy/ether, epoxy/hydroxyl, epoxy/ester,  
25 epoxy/amine, ether/amine, and cycloaliphatic  
26 ether/hydroxyl group. These compounds contain  
27 aliphatic and/or cycloaliphatic groups. Examples  
28 include Octyl Epoxy Tallate (Argus Chemical and Union  
29 Carbide), Epoxyprene 25 and 50 (Epoxidized Natural  
30 Rubber from Guthrie Latex), Epon (Epoxidized Bisphenol  
31 A from Shell Oil Co.), Styrene Oxide (S500-6 Aldrich  
32 Chemical Co.) and 1,2-Epoxy-3-phenoxypropane (24,848-7  
33 Aldrich Chemical Co.). Epoxidized plant(or vegetable)

1 oils, such as epoxidized soybean oil © P Hall PARAPLEX  
2 G62, Argus Chemical, Union Carbide and Harwick  
3 Standard) and epoxidized linseed oil (Argus Chemical),  
4 are most preferred.

5 The additive/processing aid is preferably added to  
6 polymeric materials such as rubber elastomers or  
7 plastic materials such as polyethylene, ethylene  
8 propylene. The preferred rubber elastomers are  
9 selected from the group consisting of natural rubber,  
10 isoprene, chloroprene, halo-butyls, SBR rubber, butyl  
11 rubber, neoprene, epichlorohydrin rubber,  
12 polysulfonated rubber, silicone rubber and mixtures  
13 thereof.

14 These and other aspects of the invention are  
15 described below in further detail, the illustrated  
16 embodiments being representative of only some of the  
17 ways in which the principles and concepts on the  
18 invention can be executed and employed.

19 DETAILED DESCRIPTION OF  
20 PREFERRED AND ALTERNATE EMBODIMENTS

21 The present invention is directed to an  
22 additive/process aid to facilitate the production  
23 processing of rubber elastomers. Once added to the  
24 rubber elastomers, the process aid tends to increase  
25 tensile strength, elasticity, and tear strength of  
26 these rubber elastomers.

27 The present invention is both an additive and a  
28 process aid. It is an additive because it is part of  
29 the final rubber product made by an end user. It is  
30 also considered a processing aid because the additive  
31 will aid dispersion and give the end user enhanced

1 properties associated with homogeneity as well as more  
2 through-put of product in a manufacturing process.

3 Generally, it is desirable to prepare the  
4 additive/processing aid within the preferred ranges of  
5 ingredients. Deviations from these ranges may be  
6 readily determined by designed compound evaluations  
7 measured by the obtained properties. Although  
8 deviations from these ranges may occur with trade-off  
9 of various properties, the following observations have  
10 been made rubber elastomers and additive/process aids  
11 including gray slate flour, corn starch, liquid  
12 polyester, calcium carbonate and silica gel.

13 Gray slate flour will typically be used in the  
14 range of between 20 and 30%. It is preferable to stay  
15 within this range since adding an excessive amount of  
16 gray slate flour may cause scorching of the  
17 additive/process aid and adding too little gray slate  
18 flour causes the additive/process aid to exhibit a low  
19 cure state or level of cure. Preferably, about 29 to  
20 30% by weight of gray slate flour is added to the  
21 additive/process aid. Gray slate flour helps to aid in  
22 the reinforcement of the additive/processing aid.  
23 Preferably, the gray slate flour has a particle size in  
24 the range of 32 microns. Suitable commercially  
25 available sources of gray slate flour include KeyStone  
26 Corporation, sold under the name Gray Slate Flour.

27 Further, the additives/process aid should include  
28 about 18 to 30% by weight of corn starch. Again, an  
29 excess of corn starch tends to cause scorching of the  
30 additive/process aid and a deficiency of corn starch  
31 may cause the additive/process aid to exhibit a low  
32 degree of cure. Preferably, about 28 to 30% by weight  
33 of corn starch is added to the additive/process aid.



1 Corn starch tends to increase the tear strength  
2 enhancements of the additive/process aid. Preferably,  
3 unhydrolyzed corn starch is added to the  
4 additive/process aid. A suitable corn starch is  
5 marketed by American Maze Corporation under the  
6 designation Unhydrolyzed Corn Starch.

7 The additive/process aid also comprises at least  
8 4% by weight and up to about 8% by weight of liquid  
9 polyester. It is preferred to observe this range since  
10 too much polyester tends to inhibit the incorporation  
11 of the additive/process aid into the rubber. On the  
12 other hand, if too little of the polyester is used,  
13 scorching of the product tends to occur. Liquid  
14 polyester helps to aid in the reinforcement of the  
15 additive/process aid. Preferably, the liquid polyester  
16 is clear when added to the additive/process aid.  
17 Suitable commercially available sources of liquid  
18 polyester include Dynatron Corporation of Atlanta,  
19 Georgia, the product being sold with the designation  
20 Liquid Polyester Resin.

21 Calcium carbonate should be included in the  
22 additive/process aid in accordance with the preferred  
23 ranges of from about 10% to about 35% by weight.  
24 Permissive ranges of calcium carbonate vary from 5 to  
25 70% by weight as indicated in the "high" and "low"  
26 compositions described above. However, excessive  
27 amounts of calcium carbonate may tend to cause  
28 scorching of the additive/process aid and, too little  
29 calcium carbonate, may result in a low degree of cure  
30 of the additive/process aid. Preferably, about 20% to  
31 about 40% by weight of calcium carbonate is used, and  
32 more preferably, from about 32% to about 37% by weight  
33 is used. Calcium carbonate improves the dispersion of

1 the additive/process aid. Preferably, calcium  
2 carbonate is in a white form when added to the  
3 additive/process aid. Calcium carbonate is available  
4 from the Akrochem Company and from the J. Huber  
5 Company, under the name Snowwhite Calcium Carbonate.

6 The silica gel should also be used in the  
7 preferred 8 to 15 % by weight range. Excess of amounts  
8 of silica gel tend to cause scorching on the  
9 additive/process aid and, too little silica gel, tends  
10 to result in a low degree of cure. Preferably about  
11 15% by weight of silica gel is used. Silica gel may be  
12 added in the form of pellets or powder. Silica gel  
13 helps to absorb water from the additive/process aid and  
14 promotes more uniform dispersion. Preferably, the  
15 silica gel is in a white form when added to the  
16 additive/process aid. Silica gel may be obtained from  
17 U.S. Silica Corporation under the name Minsil Silica  
18 Gel.

19 The additive/process aid of the present invention  
20 is prepared as a slow speed, mixer blend. The  
21 components of the additive/process aid are added  
22 together and mixed, and reacted under suitable time and  
23 temperature conditions. Preferably, these components  
24 are cured for 12 minutes at 307°F.

25 The additive/process aid of the present invention  
26 provides many advantages when added to a elastomeric  
27 material such as a rubber elastomer, including improved  
28 mixing, extrusion and processing characteristics, and  
29 improved tear strength. It also maintains shore A  
30 hardness and the cure state of the rubber elastomer.  
31 Further, it increases tensile strength and elasticity  
32 giving the rubber elastomer more flexibility. Finally,

1 it is a simple, low-cost additive/process aid, which  
2 consistently produces a stable product.

3 The additive/process aid is preferably added to  
4 rubber elastomers selected from the group consisting  
5 of: natural rubber, isoprene, chloroprene, halo-butyls,  
6 SBR rubber, butyl rubber, neoprene, epichlorohydrin  
7 rubber, polysulfonated rubber, silicone rubber and  
8 mixtures thereof. The rubber elastomers find  
9 particular utility for tires, tire trends, carcasses  
10 and sidewalls, coating stocks, hoses, belting, inner  
11 tubes, inner liners, general-purpose rubbers and other  
12 uses.

13 The additive/process aid is preferably added to  
14 the rubber elastomer in the range of at least 1 phr and  
15 up to 50 phr with consideration of the relative parts  
16 of ingredients contained in the additive/process aid  
17 itself. Preferably, the additive/process aid is added  
18 to the rubber elastomer in the range of from at least 2  
19 phr and up to 30 phr.

20 The present invention is further exemplified in  
21 the following examples which illustrate the use of the  
22 additive/process aid in a typical rubber compounding  
23 recipe. It is understood that the examples are only  
24 illustrative of preferred embodiments according to the  
25 present invention wherein the claims set forth the  
26 scope of the present invention.

#### 27 EXAMPLE A

28 The ASTM 297 Test Recipe for Truck Tread Tires was  
29 carried out, the resultant rubber elastomer from this  
30 test was prepared having the formulation shown in Table  
31 I.

TABLE I

1	2 RUBBER TEST RECIPE 3 Ingredients	Parts per Hundred of Rubber
4		
5	1. Natural Rubber (RSS or SMR-5)	53.6
6	2. cis-polybutadiene	13.4
7	3. napthenic process oil	36.0
8	4. stearic acid	2.0
9	5. zinc oxide	5.0
10	6. N-660 Black	10.0
11	7. nonox ZA	2.0
12	8. Santocure	0.8
13	9. Sulfur	2.0
14	10. Process Aid of Present Invention	30.0

15 The Rubber Test Recipe: First, rubber breakdown on a  
16 mill is performed. Then, each powder-based ingredients  
17 listed in Table I is added to the rubber mill, one at a  
18 time, until all are incorporated, including the  
19 additive/process aid of the present invention. The  
20 additive/process aid of the present invention comprises  
21 about 29% by weight of gray slate flour, about 28% by  
22 weight corn starch, about 8% by weight of liquid  
23 polyester, about 20% by weight of calcium carbonate,  
24 and about 15% by weight of silica gel. Then, if there  
25 are any oil-based ingredients listed in Table I, these  
26 ingredients are mixed in last. Finally, the end  
27 product is allowed to mill at least eight minutes.

COMPARATIVE EXAMPLE ONE

28  
29 A rubber elastomer was prepared having the  
30 formulation shown in Table II.

TABLE II

1	RUBBER TEST RECIPE Ingredients		Parts per Hundred of Rubber
2	3	4	
5	1. Natural Rubber (RSS or SMR-5)	53.6	
6	2. cis-polybutadiene	13.4	
7	3. napthenic process oil	36.0	
8	4. stearic acid	2.0	
9	5. zinc oxide	5.0	
10	6. N-660 Black	20.0	
11	7. N-990 Black	35.0	
12	8. nonox ZA	2.0	
13	9. Santocure	0.8	
14	10. Sulfur	2.0	

15 The rubber elastomer composition was again prepared as  
16 described above, in Example A.

COMPARATIVE EXAMPLE III

17  
18 A rubber elastomer was prepared having the  
19 formulation shown in Table III.

TABLE III

20	RUBBER TEST RECIPE Ingredients		Parts per Hundred of Rubber
21	22	23	
24	1. Natural Rubber (RSS or SMR-5)	53.6	
25	2. cis-polybutadiene	13.4	
26	3. napthenic process oil	36.0	
27	4. stearic acid	2.0	
28	5. zinc oxide	5.0	
29	6. N-660 Black	20.0	
30	7. nonox ZA	2.0	
31	8. Santocure	0.8	
32	9. Sulfur	2.0	
33	10. Silica 233	55.0	

34 The rubber elastomer composition was again prepared as  
35 described above, in Example A.

1        Once these three rubber elastomer compositions  
2        were prepared, laboratory tests were run, using ASTM  
3        297 test methods on each of the rubber elastomer  
4        compositions. The tests were designed to test specific  
5        physical characteristics, such as tensile strength, %  
6        elongation, and crescent tear of the rubber elastomer  
7        compositions. The results of each of the tests  
8        performed on each of the Example rubber elastomers are  
9        listed in the tables below.

Tensile strength is a measure of the force at which a rubber elastomer can be expected to fail under a tension load. The tensile strength of the rubber elastomer is important in order to maintain its elasticity. It is often desirable that reinforcing agents are added to natural and synthetic rubbers to increase tear strength.

TABLE IV

18	TENSILE STRENGTH	psi
19	Examples	
20	1. Example A	2750
21	2. Comparative Example One	2500
22	3. Comparative Example Two	2450

Percent elongation is a measurement of the stiffness of rubber. The higher the number, the harder the rubber composition to flux. It is often desirable that to add reinforcing agents to natural and synthetic rubbers to increase the percent elongation.

TABLE V

1		
2	PERCENT ELONGATION	
3	Examples	percent
4	1. Example A	535%
5	2. Comparative Example One	500%
6	3. Comparative Example Two	489%

7        Shore A hardness is a measure on the hardness of  
8 rubber. It also provides or indicates the cure state  
9 of a rubber composition. It is often desirable to and  
10 the reinforcing agents to natural and synthetic rubbers  
11 to maintain the Shore A hardness.

TABLE VI

12		
13	SHORE A HARDNESS	
14	Examples	Shore A hardness
15	1. Example A	61
16	2. Comparative Example One	61
17	3. Comparative Example Two	58

18        Crescent tear or tear strength is the force  
19 necessary to propagate a crack or tear under stress on  
20 a horizontal pull. It is often desirable to add  
21 reinforcing agents to natural and synthetic rubbers to  
22 increase tear strength.

TABLE VII

23		
24	CRESCENT TEAR	
25	Examples	Lb/inch
26	1. Example A	690
27	2. Comparative Example One	650
28	3. Comparative Example Two	632

29        Tan delta is a measure of the rolling resistance.  
30 The lower the reading or tan delta value, the lower the  
31 rolling resistance. It is often desirable to add

1 reinforcing agents to natural and synthetic rubbers to  
2 decrease the tan delta.

3 TABLE VIII

4	TAN DELTA	
5	Examples	resistance
6	1. Example A	0.162
7	2. Comparative Example One	0.179
8	3. Comparative Example Two	0.192

9       The results of the rubber elastomer compositions  
10 in Comparative Examples One and Two were compared to  
11 Example A for changes in the physical properties  
12 exhibited by the two rubber elastomer compositions. As  
13 apparent from the above data, use of the  
14 additive/process aid of the present invention (Example  
15 A) resulted in significant increases in tensile  
16 strength, percent elongation and crescent tear and  
17 reduced tan delta measurements. Moreover, this rubber  
18 elastomer composition also maintained its Shore A  
19 hardness measurement. Accordingly, the  
20 additive/process aid of the present invention imparts  
21 favorable properties when utilized in association with  
22 rubber elastomers.

23       Additionally, Example A contains the  
24 additive/process aid of the present invention; it does  
25 not contain large quantities of other additives/process  
26 aids, such as silica or carbon black, as compared to  
27 Comparative Examples One and Two. Thus, the improved  
28 physical characteristics of the rubber elastomer  
29 composition (Example A) are solely attributable to the  
30 additive of the present invention.

31       The additive/process aid including epoxidized oil  
32 and fatty acid is illustrated hereinafter. In a



1 preferred formulation, the additive/process aid  
2 includes the following ingredients.

3 ADDITIVE/PROCESS AID COMPOSITION

4		DB6
5	Ingredient	(Wet. %)
6	gray slate flour	25
7	corn starch	25
8	epoxidized soybean oil	5
9	calcium carbonate	35
10	stearic acid	10

11 In accordance with the foregoing additive/process aid  
12 formulation, a rubber elastomer composition Example B  
13 in accordance with the invention was prepared together  
14 with a Comparative Example Three or Control 3 as  
15 reported in the following Table IX.

16 TABLE IX

17		EXAMPLE B	CONTROL 3
18		PER	PER
19	<u>MATERIAL</u>		
20	Natural Rubber (SMR20)	30.0	30.0
21	SBR 1520	70.0	70.0
22	Carbon Black (N339)	50.0	50.0
23	DB6	2.0	0.0
24	Sunder 750 T	10.0	10.0
25	Antioxidant (Santoflex 134)	2.0	2.0
26	Stearic Acid	2.0	2.0
27	Zinc Oxide	2.5	2.5
28	Akrowax 5030	2.0	2.0
29	Sulfur	2.0	2.0
30	Accelerator CBS <sup>1</sup>	1.7	1.7
31	Co-accelerator DPG <sup>2</sup>	0.2	0.2
32	Final Total	174.4	172.4
33			
34	<sup>1</sup> N-Cyclohexyl-benzothiazolesulfenamide		
35	<sup>2</sup> Diphenylguaidine		

36 Mix Cycle: Example B and the Control were mixed in the  
37 same manner except for the inclusion of DB6 in Example  
38 B. Accordingly, the rubber and carbon black together

1 with DB6 in the case of Example B were mixed for 1.5  
2 minutes at 60 RPM in a mixer preheated to 250°F. Oil  
3 followed by Santoflex 134, stearic acid, zinc oxide and  
4 Akrowax 5030 were added, and mixing continued to a  
5 total mix time of 5.5 minutes. Then, the batches were  
6 dumped, formed into sheets on a two roll mill and  
7 allowed to cool.

8 Finish Cycle: The masterbatch followed by CBS, DPG and  
9 sulfur are combined in a mixer preheated to 175°F and  
10 mixed at 50 RPM for one minute or temperature increase  
11 to 200°F, whichever came first. Each of the rubber  
12 elastomers was then provided with 10 roll passes on a 2  
13 roll mill followed by one cut pass.

14 The compositions of Example B and Comparative  
15 Example Three were tested and the results are reported  
16 below in Table X.

17 TABLE X

18		Example B	Control 3
19	<u>Processability Testing</u>		
20	Mooney Viscosity ML4@ 212°F	54	51
21	Monsanto Rheometer		
22	Minimum Torque, m-g	93.1	98.7
23	Maximum Torque, m-g	11.8	11.2
24	Scorch, t1, min.	5.67	5.67
25	90% Cure Time min.	13.83	13.00
26	<u>Physical Properties</u>		
27	<u>Stress-Strain Properties</u>		
28	Room Temperature 23°C		
29	50% Modulus, psi	285	259
30	100% Modulus, psi	573	510
31	200% Modulus, psi	1490	1351
32	300% Modulus, psi	2539	2368
33	Tensile Strength, psi	3042	2928
34	Elongation, %	351	357

TABLE X Cont.

1			
2	Elevated Temperature 100°C		
3	50% Modulus, psi	275	244
4	100% Modulus, psi	554	484
5	200% Modulus, psi	1301	1182
6	300% Modulus, psi	-	-
7	Tensile Strength, psi	1404	1449
8	Elongation, %	219	228
9	Shore A Hardness		
10	Room Temperature 23°C	70	70
11	Elevated Temperature 100°C	-	-
12	Tear Strength ASTM D624 Die C		
13	Room Temperature 23°C	193	190
14	Elevated Temperature 100°C	102	118
15	Bashore Resilience, %	41	41
16		62	60
17	<u>Dynamic Properties 1 Hz</u>		
18	5% Compression		
19	Elastic Modulus, E'		
20	26°C	8.05x10 <sup>6</sup>	7.60x10 <sup>6</sup>
21	75°C	6.63x10 <sup>6</sup>	6.33x10 <sup>6</sup>
22	122°C	6.05x10 <sup>6</sup>	5.85x10 <sup>6</sup>
23	Storage Modulus, E''		
24	26°C	1.80x10 <sup>6</sup>	1.79x10 <sup>6</sup>
25	75°C	1.08x10 <sup>6</sup>	1.08x10 <sup>6</sup>
26	122°C	0.812x10 <sup>6</sup>	0.768x10 <sup>6</sup>
27	Tangent		
28	26°C	0.223	0.235
29	75°C	0.163	0.170
30	122°C	0.134	0.131
31	10% Compression		
32	Elastic Modulus, E'		
33	26°C	6.81x10 <sup>6</sup>	6.57x10 <sup>6</sup>
34	75°C	6.04x10 <sup>6</sup>	5.71x10 <sup>6</sup>
35	123°C	5.77x10 <sup>6</sup>	5.39x10 <sup>6</sup>

TABLE X Cont.

1			
2	Storage Modulus, E"		
3	26°C	1.39x10 <sup>6</sup>	1.47x10 <sup>6</sup>
4	75°C	0.876x10 <sup>6</sup>	0.931x10 <sup>6</sup>
5	123°C	0.687x10 <sup>6</sup>	0.651x10 <sup>6</sup>
6	Tangent Delta		
7	26°C	0.204	0.223
8	75°C	0.145	0.163
9	123°C	0.119	0.121

10        The use of epoxy resin and fatty acids is further  
11 illustrated in the following Examples C and D. More  
12 particularly, Examples C and D illustrate variations in  
13 the relative amounts or proportions of the ingredients  
14 of the additive compositions in accordance with the  
15 invention. More particularly, the additive/process aid  
16 DB6H of Example C includes a lesser amount of calcium  
17 carbonate in favor of relatively high amounts of the  
18 remaining ingredients and the aid DB6L used in Example  
19 D includes a relatively higher amount of calcium  
20 carbonate with reduced amounts of the remaining  
21 ingredients as summarized below.

ADDITIVE/PROCESS AID COMPOSITIONS

22			
23		DB6H	DB6L
24	Ingredient	(Wet. %)	(Wet. %)
25	gray slate flour	30	10
26	corn starch	35	10
27	epoxidized soybean oil	15	5
28	calcium carbonate	5	70
29	stearic acid	15	5

30        Examples C and D in accordance with the invention  
31 respectively include additive/process aids DB6H and  
32 DB6L together with the additional constituents shown in  
33 the following Table IX. For comparison, a Control 4 or

1 Comparative Example Four was prepared as reported in  
2 Table XI.

3 TABLE XI

4	EXAMPLE C	EXAMPLE D	CONTROL 4
5	PER	PER	PER
6 <u>MATERIAL</u>			
7 Natural Rubber			
8 (SMR20)	30.0	30.0	30.0
9 SBR 1520	70.0	70.0	70.0
10 Carbon Black (N343)	41.0	41.0	41.0
11 DB6H	2.0	0.0	0.0
12 DB6L	0.0	6.0	0.0
13 Aromatic Oil (Shell 750)	10.0	10.0	10.0
14 Antioxidant			
15 (Santoflex 13)	1.0	1.0	1.0
16 Stearic Acid	2.0	2.0	2.0
17 Zinc Oxide	2.5	2.5	2.5
18 Akrowax 5030	1.0	1.0	1.0
19 Masterbatch Total	157.5	159.5	163.5
20 Masterbatch	157.5	159.5	163.5
21 Sulfur	1.3	1.3	1.3
22 Accelerator CBS <sup>1</sup>	1.7	1.7	1.7
23 Co-accelerator DPG <sup>2</sup>	0.2	0.2	0.2
24 Final Total	160.7	162.7	166.7

25 <sup>1</sup>N-Cyclohexyl-benzothiazolesulfenamide  
26 <sup>2</sup>Diphenylguaidine

27 Masterbatch Mixing procedure: Start temperature 250°F,  
28 RPM'S 40, add pre-blended polymers and carbon black  
29 (together with DB6H or DB6L in Examples B and C), 0  
30 minutes, mix for 1.5 minutes. Add oil followed by  
31 antioxidant, stearic acid, zinc oxide and wax, increase  
32 RPM to 60. Mix for 4 minutes and dump. Sheet out and  
33 cool.  
34 Final Mixing Procedure: Start temperature 175°F, RPM's  
35 50. Add masterbatch, followed by remaining  
36 ingredients. Mix keeping temperature below 200°F.  
37 Dropped and performed 10 cut passes and 10 roll passes  
38 on mill.

1           Examples C and D together with the Control 4 or  
2 Comparative Example Four were cured for 15 minutes at  
3 149°C and tested. The results of the tests are  
4 reported below in Table XII.

TABLE XII				
	Example C	Example D	Control 4	
7	Rheometrics @ 149°C			
8	MH	72.60	75.36	73.94
9	ML	10.52	11.74	11.13
10	TC80	14.89	13.43	13.93
11	TC90	18.13	16.75	16.77
12	TS2	8.32	7.11	7.98
13	TS5	9.63	8.20	9.24
14	Mooney Viscosity			
15	ML(1+4)@100°C	40.31	45.19	40.30
16	Shore A Hardness			
17	Hardness@23°C	55.2	55.0	55.2
18	Hardness@100°C	66.2	67.4	66.0
19	Pendulum Rebound			
20	Rebound@23°C	52.7	56.3	53.2
21	Rebound@100°C	49.6	52.8	48.8
22	Stress-Strain Properties			
23	Results at 23°C			
24	100% Modulus, psi	192	235	183
25	200% Modulus, psi	474	618	451
26	300% Modulus, psi	1031	1314	956
27	Tensile Str., psi	2814	2962	2317
28	Elongation, %	534	496	500
29	Results at 100°C			
30	100% Modulus, psi	176	211	170
31	200% Modulus, psi	401	504	385
32	300% Modulus, psi	801	984	754
33	Tensile Str., psi	1225	1247	1182
34	Elongation, %	392	351	402
35	Tear Strength			
36	Pounds/in.@23°C	556.9	427.4	463.4
37	Pounds/in.@100°C	310.7	241.6	336.4
38	Specific Gravity	1.0746	1.0659	1.0686

TABLE XII Cont.

1

2 Tangent Delta<sup>1</sup>

3 Tan Delta@ 5% strain 0.14305 0.13385 0.15172

4 % decrease from Control 5.714 11.778 na

5 Tan Delta@ 10% strain 0.13876 0.12925 0.14654

6 % decrease from Control 5.309 11.799 na

7 <sup>1</sup>(50°C, 1HZ, Strain Sweep)

8 As indicated by the foregoing comparisons, the  
9 additive/process aid in accordance with the present  
10 invention imparts increased tensile strength especially  
11 under conditions of elevated temperature and high  
12 strain. In addition, hysteresis is reduced as  
13 indicated by the decrease in the tan delta values as  
14 compared with the Control or Comparative Example Three.  
15 Reduced hysteresis is associated with reduced rolling  
16 resistance and reduced heat build-up during tire  
17 operation or other cycled loading of the rubber  
18 elastomer which give rise to lower fuel consumption  
19 and/or increased elastomer product life.

20 Although preferred embodiments have been described  
21 in detail, it should be understood that various  
22 changes, substitutions, and alterations can be made  
23 therein without departing from the spirit and scope of  
24 the invention as defined by the appended claims. It  
25 will be appreciated that various changes in the  
26 details, materials and arrangements of parts, which  
27 have been herein described and illustrated in order to  
28 explain the nature of the invention, may be made by  
29 those skilled in the area within the principle and  
30 scope of the invention as will be expressed in the  
31 appended claims.